Chapter IV Soil-Gas Surveys

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Chapter IV Soil-Gas Surveys

Soil-gas surveys are defined as the collection, analysis, and interpretation of soil-gas data. As such, soil-gas surveys provide information on the soil atmosphere in the vadose zone that can aid in assessing the presence, composition, source, and distribution of contaminants. Soil-gas surveys can provide relatively rapid and cost-effective site data that can help direct more costly and invasive techniques. Although, they are typically performed early in the expedited site assessment (ESA) process, soil-gas surveys can also be used to monitor underground storage tanks (USTs) for releases, to evaluate remediation effectiveness, and to assess upward migration of vapors into buildings for risk assessments.

There are two basic types of soil-gas surveys commonly performed during UST site assessments. The first type is the active soil-gas survey in which a volume of soil gas is pumped out of the vadose zone into a sample collection device for analysis. The second type is the passive soil-gas survey in which a sorbent material is left in the ground so that contaminant vapors can be selectively adsorbed over time using the ambient flow of soil gas. Active soil-gas surveys can be completed in as little as one day and are most commonly used for sites with volatile organic compounds (VOCs). Passive soil-gas surveys take several days or weeks to complete and are most useful where semivolatile organic compounds (SVOCs) are suspected or when soils prevent sufficient air flow for active sampling.

This chapter provides a discussion of soil-gas principles affecting soil-gas surveys, the applicability and the essential elements of both active and passive soil-gas surveys, and case studies illustrating the effective use of both soil-gas surveying methods. Details on soil-gas sampling equipment are provided in Chapter V, Direct Push Technologies, and a discussion of soil-gas analytical methods is presented in Chapter VI, Field Methods For The Analysis Of Petroleum Hydrocarbons.

Applicability Of Soil-Gas Sampling

In order to understand the applicability and design of soil-gas surveys, it is important to first understand the parameters that control the migration of contaminants through the vadose zone. The primary controlling parameters are the physical and chemical properties of the contaminant, the site geology, and biological processes. This section contains brief descriptions of these parameters, how they affect various contaminants, and how they relate to the applicability of active and passive soil-gas sampling.

Physical And Chemical Properties Of Hydrocarbons

To assess whether soil-gas sampling is applicable to characterize subsurface contamination at an UST site, the potential for the contaminant to be present in the vapor phase first needs to be evaluated. Petroleum products stored in USTs, such as gasoline, diesel fuel, and kerosene, are complex mixtures with more than 100 different compounds, each with a different degree of volatility. Therefore, individual constituents must be assessed independently. The degree to which a chemical will partition into the vapor phase is primarily controlled by the compound's vapor pressure and its Henry's law constant.

Vapor Pressure

Vapor pressure is one of the most important constituent characteristics for determining if a particular hydrocarbon can be detected as a gas in the source area. The vapor pressure of a constituent is a measure of its tendency to evaporate. More precisely, it is the pressure that a vapor exerts when it is in equilibrium with its pure liquid or solid form. As a result, the higher the vapor pressure of a constituent, the more readily it evaporates into the vapor phase. As a general rule, vapor pressures higher than 0.5 mm Hg are considered to be detectable with active methods. Occasionally, constituents with lower vapor pressures can be detected, but the soil concentrations must be high and the geological formation should be permeable. If the contaminant is dissolved in groundwater or soil moisture, Henry's law constant must be considered along with the vapor pressure to determine the potential for detection (see below). Exhibit IV-1 lists the vapor pressures of selected petroleum constituents.

Gasoline contains a number of hydrocarbons that have sufficient vapor pressures to be easily sampled with active soil-gas surveying methods. Jet fuel,

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Exhibit IV-1
Vapor Pressure And Henry's Law Constant
Of Various Organic Compounds At 20° C

Compound	Vapor Pressure (mm Hg)	Compound	Henry's Law Constant (dimensionless)
n-Butane	1560	n-Hexane	36.61
Methyl t-butyl ether	245	n-Butane	25.22
n-Hexane	121	Ethylbenzene	0.322
Benzene	76	Xylenes	0.304
Toluene	22	Toluene	0.262
Ethylbenzene	7	Benzene	0.215
_Xylenes	6	Methyl t-butyl ether	0.018
Naphthalene	0.5	Naphthalene	0.018

^{*} Values above dotted line indicate active active soil-gas sampling methods are appropriate.

diesel fuel, and kerosene contain SVOCs that can be actively sampled only under optimal conditions. Lubricating and waste oils contain mainly low volatility compounds and cannot be directly sampled through active methods. Passive sampling methods, which are more successful in detecting SVOCs, may be successful in detecting some low volatility compounds.

Henry's Law Constant (Water To Vapor Partitioning)

Henry's law constant is a measure of a compound's tendency to partition between water and vapor. This constant can be used to estimate the likelihood of detecting a constituent in the vapor phase that had dissolved in soil moisture or groundwater. There are several ways to express this constant, but the most useful way is in the dimensionless form. Henry's law constant can be obtained by dividing the equilibrium concentration of a compound in air with the equilibrium concentration of the compound in water (at a given temperature and pressure). Because the units on both values are the same, the resulting constant is dimensionless.

Compounds with a greater tendency to exist in the vapor phase have a Henry's law constant greater than 1, compounds with a greater tendency to exist in water have a Henry's law constant less than 1. Henry's law constants for several common constituents found in petroleum products are shown in Exhibit IV-1.

Notice that alkanes (chained hydrocarbons [*e.g.*, butane, hexane] commonly found in gasoline) have Henry's law constant values two orders of magnitude greater than aromatics (ringed hydrocarbons [*e.g.*, benzene, toluene]). In a state of equilibrium, 36 molecules of hexane will exist in the vapor phase for every molecule of hexane dissolved in water. Whereas, for every five molecules of benzene dissolved in water, only one will be found in the vapor phase. Consequently, if equal volumes of alkanes and aromatics have been spilled on a site, in the source area alkanes will be found in much higher concentrations in the soil gas. However, because alkanes partition out of the dissolved phase to a greater extent, aromatics are more likely to provide an indication of dissolved contaminant plumes. In addition, vapor phase concentrations of compounds such as methyl *t*-butyl ether (MTBE) or naphthalene will not be useful indicators of contamination in soil gas outside the source area because they tend to remain dissolved in water.

In general, compounds with Henry's law constants greater than 0.1 are considered to be detectable with active soil-gas sampling if the vapor pressure is also sufficient and geologic conditions are favorable. Constituents with slightly lower values may also be detectable if initial concentrations are high. Passive soil gas techniques are able to detect compounds with lower Henry's law constants, however, a precise limit of detection cannot be estimated because site conditions, exposure times, and product sensitivities will vary.

Geologic Factors

The most important geologic factor in the movement of soil gas through the vadose zone is soil permeability, a measure of the relative ease with which rock, soil, or sediment will transmit a gas or liquid. Soil permeability is primarily related to grain size and soil moisture. Soils with smaller grain sizes, and hence smaller pore spaces, are less permeable. Clays, having the smallest grain size, significantly restrict soil vapor migration.

Soil moisture decreases permeability because moisture trapped in the pore space of sediments can inhibit or block vapor flow. Since soil moisture content varies seasonally and geographically, effective air permeabilities are often unknown prior to sampling. For active soil-gas surveys, soil-air permeability

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testing should be conducted in vertical profiles at select locations in order to optimize sampling depth. For passive soil-gas surveys, soil-air permeability is important but usually not determined because additional equipment is required.

In addition, there are several other soil factors that can create misleading information about the location of contamination. Preferential pathways (*e.g.*, tree roots, soil cracks, utilities, backfill) and vapor impervious layers (*e.g.*, clay layers, foundations, buried pavement, perched groundwater) are features that should be evaluated. Moreover, adsorption of hydrocarbons on soils with high percentages of clay or organic matter can limit partitioning of contaminants into the vapor phase.

Although active soil-gas sampling is applicable for all soil types except tight clays, it is generally ineffective when the soil moisture is above 80- to 90-percent saturation (Corey, 1986) because of the absence of connected air-filled pores. High soil moisture conditions can be overcome with sampling procedures (e.g., minimizing sample volume, increasing the air volume around the tip, waiting for equilibrium to take place), but these procedures can often be very time consuming.

Passive soil-gas sampling is generally useful in all soil types and conditions, however, sediments with low intrinsic permeabilities and high degrees of saturation can affect both the quantity of contaminants coming into contact with the sampler and the quantity of contaminant that is adsorbed. For example, the presence of a dense moist clay lense will reduce the amount of vapor that contacts a sampler directly above it. In addition, Werner (1985) demonstrated that activated carbon, a common soil-gas adsorbent, will adsorb significantly less TCE with increasing relative humidity levels. Other contaminants may, therefore, also be adsorbed to a lesser degree under humid conditions. Although passive soil-gas sampling remains more sensitive to contaminant detection than active soil-gas sampling under low permeability and high humidity, geologic heterogeneities in the subsurface can also affect passive soil-gas results.

Biodegradation

Biodegradation of VOCs in the vadose zone can reduce the ability to detect the contaminants in soil gas. Petroleum hydrocarbons are readily degraded by microorganisms to produce increased levels of numerous gases (*e.g.*, carbon dioxide, hydrogen sulfide, methane) while decreasing the concentration of oxygen. The rate of biodegradation is controlled by several factors, including soil moisture content, concentration of electron acceptors (*e.g.*, oxygen) available nutrients in the soils, contaminant type, and soil temperatures.

Sampling for soil gases affected by biodegradation (*e.g.*, oxygen, carbon dioxide, methane, hydrogen sulfide) can provide useful information about the contaminant source area and plume, provided background samples are collected in a neighboring uncontaminated area. Measurement of these parameters is most useful when active soil-gas sampling is being employed and the contaminant is a semivolatile or non-volatile compound, or if a volatile contaminant is known to exist but has not been directly detected.

Summary

Detection of individual constituents by both active and passive soil-gas sampling methods is limited by the physical and chemical properties of hydrocarbons. General parameters for selecting active soil-gas sampling are presented in Exhibit IV-2. Passive soil-gas sampling methods are more sensitive than active soil-gas sampling, but individual manufacturers should be contacted for specific compounds that can be detected.

Vapor pressure and Henry's law constant are indicators of the potential of a method to detect a specific constituent. For active sampling, the vapor pressure should be above 0.5 mm Hg. If contamination is dissolved in soil moisture or groundwater, the Henry's law constant should also be above 0.1. Geologic factors (e.g., clay layers, high soil moisture content) will affect both active and passive sampling capabilities, but passive sampling will generally provide more sensitive results under these conditions. In addition, the byproducts of biodegradation can provide valuable information in active soil-gas sampling for indirect detection of contaminants.

Exhibit IV-2 Summary Of General Active Soil-Gas Sampling Criteria*

Vapor Pressure > 0.5 mm Hg

Henry's Law Constant > 0.1

Degree Of Saturation < 80%

Sampling Zone Is Free Of Clay

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^{*} Active sampling may still be useful for the indirect detection of contaminants below these vapor pressure and Henry's law constant values.

Active Soil-Gas Sampling Methods

Of the two soil-gas sampling methods—active and passive—active soil-gas sampling is the method typically used for site investigations where VOCs are the primary constituents of concern. This method allows for rapid soil-gas collection from specific depths by analyzing soil gas that has been pumped from the ground through probe holes. The samples are typically analyzed on-site so that real-time data can be used to direct further sampling. VOCs can be detected directly with soil-gas sampling methods, while SVOCs and low volatility organic compounds may be detected indirectly through the measurement of gases (O₂, CO₂, H₂S, CH₄) influenced by biogenic processes.

Active soil-gas surveying was initially utilized by the oil industry in the 1960s to monitor gas control systems, track gas migration off-site, and evaluate resources. It was first applied to VOC site assessments in the early 1980s and rapidly gained popularity as a screening tool to detect and delineate subsurface contamination.

Samples are collected by inserting a sampling device into a borehole, usually with a slam bar, a direct push system, or a hollow stem auger. Most sampling devices consist of screens or ports that are pushed directly into the ground or inserted through the insides of drill rod or pipe. Soil gas is drawn through the port or screen through plastic (primarily polyethylene or TeflonTM) or metal tubing and into a collection vessel using a vacuum device. The port or screen, tubing, sample vessel, and vacuum source are collectively referred to as the "sample train." For a more detailed discussion of soil-gas sampling equipment refer to Chapter V, Direct Push Technologies.

As active soil-gas sampling has evolved and become more cost effective through the application of direct push technology, on-site analysis of soil-gas samples by mobile laboratories utilizing transportable gas chromatographs has become more common. Mobile laboratories provide quantitative chemical data with rapid turnaround time and do not necessitate the packaging and shipping of samples. Other useful pieces of analytical equipment include total organic vapor detection instruments, such as photoionization detectors (PID) and flame ionization detectors (FID), field portable gas chromatographs, and detector tubes. Assessment objectives must be considered in the selection of analytical methods because capabilities and limitations are extremely variable. A detailed discussion of analytical methods for soil-gas analysis is provided in Chapter VI, Field Methods For The Analysis Of Petroleum Hydrocarbons.

Applications For Active Soil-Gas Sampling

Active soil-gas sampling can be an important aspect of an ESA because it provides the ability to assess many different aspects of a site in a short period of time, typically in 1 to 3 days. Active soil-gas sampling can help the investigator:

- Identify releases;
- Identify sources of contaminants;
- Identify the types of VOCs present in the vadose zone;
- Provide an indication of the magnitude of VOC and SVOC contamination;
- Infer contaminant distribution of SVOCs and low volatility organic hydrocarbons by measuring indicators of biodegradation;
- Optimize the placement of soil borings and monitoring wells;
- Monitor potential off-site sources;
- Collect data that could be useful in the design of soil vapor extraction (SVE) or bioventing systems;
- Assess the potential for upward migration of vapors in buildings; and
- Monitor the effectiveness of remedial systems.

One major advantage of active soil-gas sampling is that data can be collected from discrete depths for vertical profiling of contaminant concentrations and relative air permeabilities in the vadose zone. This information helps to provide a 3-dimensional conceptualization of the contaminant distribution and allows for calculation of upward and downward contaminant fluxes.

Active Soil-Gas Survey Design

Although active soil-gas surveys are a rapid and effective way to focus subsequent assessment methods, several procedures are needed to ensure that the data provided are valid. The following section describes some of the essential elements required for a successful active soil-gas survey.

Review Existing Site Information

Investigators should review and evaluate existing site information in order to make an initial determination of the applicability of active soil-gas sampling (refer to previous section). If active sampling is appropriate, this information will also help the investigator select sampling locations. Information to be reviewed may include:

• Type of contaminant and suspected release mechanism (e.g., spills, leaks);

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- Estimates of volume of contaminant discharged;
- Length of time contaminant has been present;
- Stratigraphy of the site;
- Depth of groundwater, direction and rate of flow;
- Map of site facility with subsurface structures (*e.g.*, tanks, sewers, piping, wells): and
- Reports of site inspections.

Preliminary Measurements For Soil-Gas Sampling

There are three conditions that should be assessed prior to sampling, to determine how soil-gas samples should be extracted and to ensure that the samples are representative of subsurface conditions: Relative soil-air permeability, purge volume and rates, and subsurface short circuiting.

Relative Soil-Air Permeability Testing

Relative soil-air permeability can help to assess the influence of geologic materials and the moisture content at the locations tested. An estimate can be calculated by comparing air flow data with the corresponding vacuum pressure or more accurately by using a pressure transducer. Low permeability zones should be identified to help interpret the data.

Purge Volume And Rates

Prior to initiating sampling at a site, tests should be conducted to optimize the purge volume and rates. Generally, these tests should be conducted in various soil types encountered at the site and in the areas of suspected elevated VOC concentrations. The tests are performed by varying the purge volume and rates at a single location while samples are being taken. Optimal sampling conditions occur when contaminant concentrations stabilize.

Subsurface Short Circuiting

Purge volume and rate tests should also be used to check for subsurface short circuiting with the above-ground atmosphere. This condition is indicated when contaminant levels decrease rapidly or when atmospheric gases (*e.g.*, atmospheric oxygen levels) are detected. Sometimes indicator VOCs (*e.g.*, pentane) are placed on a rag near the probe hole. In order to prevent short

circuiting, it is important to seal the probe hole, typically with wet bentonite. In addition, the drive-point should not be larger than the diameter of the probe because the open space created by the drive-point would provide a conduit for atmospheric gases to travel.

Initial Sampling

Initial sampling points are usually located in potential source areas. The proposed sampling locations should be located on a facility map with subsurface structures noted. Additional sampling points need to be considered along possible conduits (*e.g.*, sewer lines, trenches, utility vaults, pipelines) where contaminants may preferentially migrate. Sampling may also be organized along a standard orthogonal grid.

Sampling Depth

The depth of sampling will vary depending on the depth to groundwater and the stratigraphy of the site. Active soil-gas sampling in a vertical profile is necessary to determine the permeable horizons and vertical contaminant distributions. Initial profiles should be completed in known or suspected source areas and in areas where elevated VOCs are detected. If liquid phase hydrocarbon delineation is the objective, soil-gas surveys should be collected just above the water table.

Sample Spacing

Sample spacing depends primarily on the objectives of the investigation, the size of the site, and the size of potential contaminant sources. At 1- or 2-acre USTs sites, initial spacing is generally between 10 and 50 feet. When trying to track down the source at a major industrial site, spacing may be as great as 400 or 500 feet. Sufficient soil-gas data from shallow and deeper vadose zone horizons should also be collected to provide a 3-dimensional distribution of the contaminants. The spacing between vertical samples depends primarily on the depth to groundwater and the objectives of the investigation. Data should be integrated into maps and contoured in the field to determine if additional sampling locations are necessary. As a general rule, if two sampling points have a 2 to 3 orders of magnitude change, samples should be collected in the area between the two points.

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Sample Containers

There are four commonly used sample containers, each with different advantages and limitations. Stainless steel canisters are durable, but they can be difficult to decontaminate. Glass bulbs are easy to decontaminate, but they are breakable and may have leakage through the septa. Tedlar® bags are easy to handle and leakage is readily apparent, but some contaminants may sorb onto the bag (for the primary gasoline constituents, however, this is not a problem). Syringes are inexpensive and allow for easy collection of samples, but they have short holding times and are difficult to decontaminate. Although no sampling container is perfect, problems are minimized by analyzing samples as soon as possible after collection.

Quality Assurance/Quality Control Procedures

There are numerous QA/QC procedures that must be undertaken during an active soil-gas survey to ensure that the samples are representative of subsurface conditions. The following list is not comprehensive for all site conditions or equipment; rather, it contains the primary issues that regulators should check when they evaluate active soil-gas survey reports. QA/QC procedures include:

- All soil-gas surveys should be collected following the same procedures.
- Sampling should be completed in a relatively short period of time (*e.g.*, hours, days) because temporal variations such as temperature, humidity, barometric pressure, and rain can affect contaminant concentrations.
- Decontamination procedures should be practiced to prevent contaminant gain or loss that results from adsorption onto sampling equipment.
- The insides of the sample train components should be as dry as possible because water can raise or lower contamination values.
- Ambient air present in the sample train must be purged prior to sample collection.
- When sampling directly through probe rods, the sample train connections should be checked prior to collecting each sample to ensure they are airtight.
- Annular space between the side of the borehole and the installation device (*e.g.*, probe rod) should be sealed at the ground surface with a bentonite paste or similar material.
- Blank samples should be tested regularly to ensure that decontamination procedures are adequate and to determine background VOC levels.
- Duplicate soil-gas samples should be collected each day (generally 1 for every 10 samples) to assess the reproducibility of the data.
- Sample containers should be monitored for leakage.

Interpretation Of Active Soil-Gas Data

A thorough understanding of the capabilities of the active soil-gas sampling methods and the site conditions is necessary for avoiding over-interpretation of the soil-gas survey results. Soil-gas concentrations must be compared with stratigraphic and cultural features in order to determine how soil-gas migrates and how contaminants are distributed. Subsurface barriers (*e.g.*, clay lenses, perched groundwater, infrastructure, buildings) and secondary pathways (*e.g.*, utility trenches, animal burrows) can cause soil-gas distribution to be significantly different than soil and groundwater contamination. As a result, stratigraphic cross-sectional maps should be used to evaluate vertical concentrations. Trends noted should be evaluated to assess whether they are associated with soil types, chemical migration, influence of diffusion from groundwater, potential preferential pathways, or obstructions.

Interpretation of the soil-gas data should begin in the field. Posting the data on a site map as the results are reported will help to direct and refine the sampling program. The final results of the soil-gas survey are usually presented in maps showing contours of gas concentrations at various subsurface depths. Sample depths should be corrected for site elevation changes so that the contour represents a horizontal layer. By creating several horizontal contours, data can be analyzed in 3-dimensions. Plotting total VOCs is often the easiest method, but it is important to evaluate if differing sources exist by examining the distribution of individual constituents.

An example of this type of analysis is the use of the ratio between prebenzene hydrocarbons (*i.e.*, constituents that pass through a gas chromatograph column prior to benzene) to total VOCs to determine the relative length of time a contaminant has been present. Since the pre-benzene constituents of gasoline migrate more rapidly than other hydrocarbons, a relatively high ratio will indicate a more recent release while a low ratio will indicate an older release. Because there are many factors that affect the absolute ratio, the ratios can only be used to compare multiple releases at a single site.

An additional issue that is important for interpretation of results is analysis of the units of measurement. Commonly, two types of units are used for reporting soil-gas data: Volume per volume (e.g., ppm $_v$ or ppb $_v$) or mass per volume (e.g., $\mu g/l$ or mg/m 3). Although for water, $\mu g/l$ is equivalent to ppb, this is not true for gases. If concentrations are reported in $\mu g/l$, a conversion may be required. For samples analyzed at 20 $^{\circ}$ C and 1 atm pressure:

$$ppb_v = \mu g/l$$
 x $\frac{2.447 \times 10^4}{molecular weight of the gas}$.

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Costs Of Active Soil-Gas Surveys

Because the sampling and analytical equipment used in active soil-gas surveys varies considerably according to the site conditions, the survey objectives, and the investigator preferences, the cost will also vary considerably. Most soilgas surveys are performed using direct push (DP) technology. The cost of collecting active soil-gas surveys with truck mounted DP ranges from \$1,000 to \$2,000 per day. In some cases, DP can be deployed manually, which may be less expensive. Typically, 10 to 30 samples can be collected per day depending primarily on soil type, sampling depths, and sampling method. Numerous field analytical methods are applicable for soil-gas surveys (listed in Chapter VI, Field Methods For The Analysis Of Petroleum Hydrocarbons), however, portable and transportable gas chromatographs are most common because of their high data quality level capabilities. Samples are rarely sent off-site to a fixed laboratory because on-site information is often used for determining subsequent sample locations and delays in analysis can affect data quality. Active soil-gas survey sampling can be completed in as little as 1 day at a 1-acre site and should rarely require more than 3 days. As a result, the cost of a complete soil-gas survey with a report will typically range from \$3,000 to \$15,000.

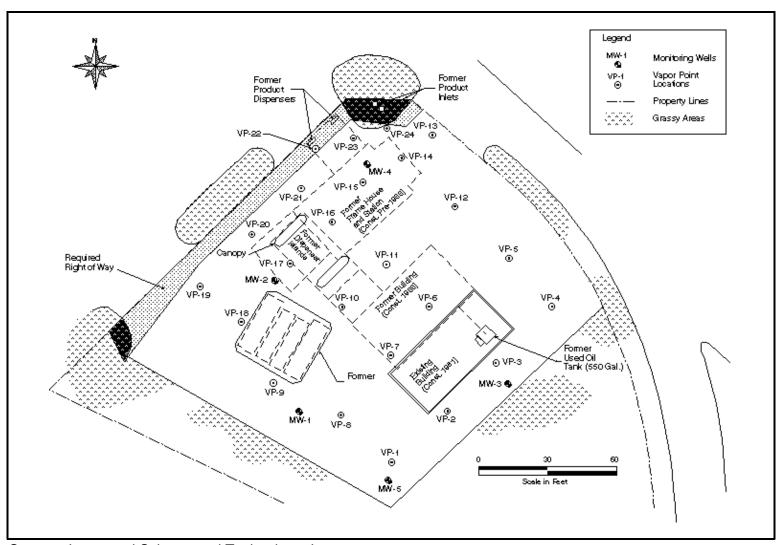
Active Soil-Gas Survey Case Study

The following case study provides an example of the type of data that can be collected with an actual active soil-gas survey at an UST site and how it may be interpreted. A map of the site described in this case study, including the vapor point and monitoring well locations, is presented in Exhibit IV-3.

Site History

In 1966, a retail gasoline marketing company purchased an UST facility from an independent dealer. The facility had been operated as a gasoline station for an undetermined period of time; there were an unknown number of USTs on the property. The company reconstructed the facility shortly after the purchase date and remodeled in 1981. In 1991, the site was closed, and the tanks were removed. In order to remove petroleum-stained soil, the tank pit and piping trenches were over-excavated. Five monitoring wells were installed to determine if groundwater had been contaminated. The results indicated that groundwater remained uncontaminated; however, a high degree of soil contamination was discovered in MW-4, and significantly less contamination was discovered in MW-1. In addition, monitoring well data indicated that the water table was located at approximately 21 feet and the gradient flowed to the south.

Exhibit IV-3
Active Soil-Gas Survey Site Map With Vapor Point And Monitoring Well Locations



Source: Integrated Science and Technology, Inc.

Soil-Gas Survey Objective

The main objective of the survey was to determine the risk of contaminant migration. Emphasis was placed on source identification and delineation because of the multiple ownership history of the facility and the potential for multiple responsibilities for the contamination.

Sampling And Analytical Methods

The site was divided into a grid with spacing of 30 feet by 30 feet. Twenty-four sampling locations were established, providing comprehensive areal site coverage. A small-diameter steel probe sampler with a slotted terminal end was driven into the subsurface with a mechanical hand-held hammer. An electric vacuum pump was used to purge the system for 5 minutes prior to sampling. Samples were collected with a gas-tight glass syringe and immediately analyzed with a field portable GC/PID.

In order to assess the soil heterogeneities, vertical profiling was performed at all 24 locations. Sampling depths were at 3, 6, 9, 12, 15, and 18 feet. When no significant contamination was indicated, samples were only taken at the first two or three levels. A total of 87 samples was collected and analyzed over 3 days.

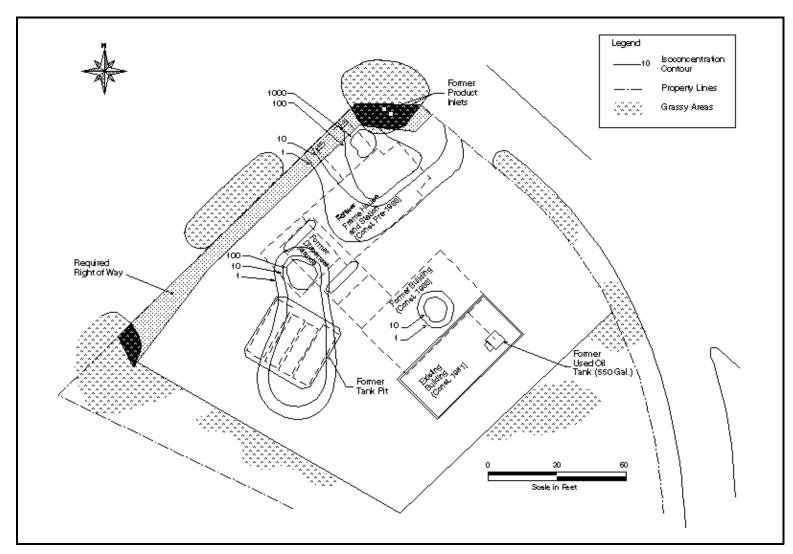
Results and Discussion

An evaluation of the vertical profiles indicated that the site geology was relatively homogenous, permeable, and appropriate for active soil-gas sampling. Short circuiting of the above-ground atmosphere was determined to not have affected the data. In total, all QA/QC procedures supported the validity of the data collected.

Exhibits IV-4 and IV-5 present the isoconcentration contours for total volatiles at 9 and 12 feet, respectively. The data indicated three separate areas of contamination. Most of the hydrocarbons were located at the north end of the station, directly under the former operation area (pre-1966). A smaller zone of contamination was located just north of the existing building and at the northwest side of the site, next to existing product line trenches. Multi-level sampling proved very useful at this site because if samples had been collected from only one level, only one release would likely have been identified.

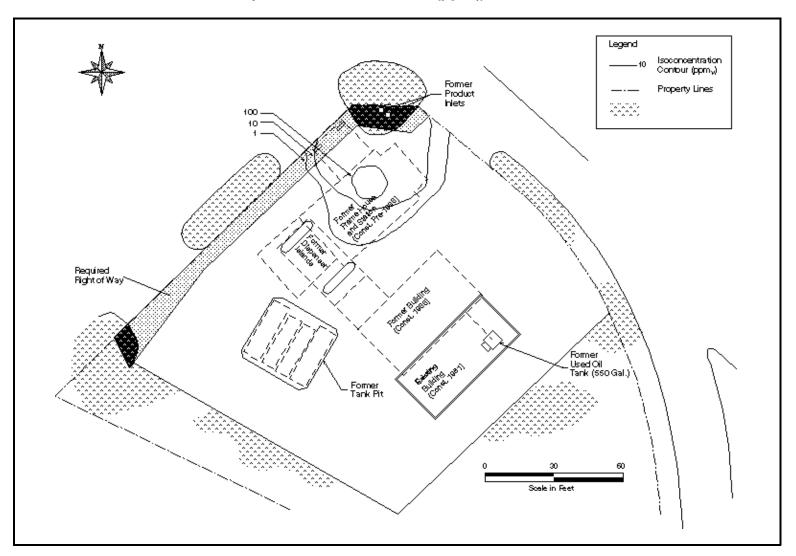
The absolute hydrocarbon vapor concentrations indicated the presence of moderately high levels of soil residual hydrocarbons, especially in the north

Exhibit IV-4 Active Soil-Gas Survey Plot Of Total Volatiles (ppm_v) Isoconcentrations At 9 Feet



Source: Integrated Science and Technology, Inc.

Exhibit IV-5
Active Soil-Gas Survey Plot Of Total Volatiles (ppm_v) Isoconcentrations At 12 Feet



Source: Integrated Science and Technology, Inc.

corner of the facility. The measurements at the 15 and 18 feet depth were lower than would be expected if floating product existed on the water table. In addition, the pre-benzene to total VOC ratio was examined for each sample to determine the relative age of the source areas. The data indicated that the source area in the north corner was significantly older than the other two areas. This evidence suggested that there were at least two—and possibly three—separate source areas.

Because the oldest and largest source area had been present for at least 25 years without contamination reaching the groundwater, and because there were no sensitive receptors in the vicinity, the state regulator determined that further remediation of this site was not necessary.

A summary of the advantages and limitations of active soil-gas surveys is presented in Exhibit IV-6.

Exhibit IV-6
Advantages And Limitations Of Active Soil-Gas Sampling

Advantages	Limitations
Samples can be analyzed on site for "real time" data reporting.	Not effective for identifying SVOCs or low volatility compounds.
From 10 to 30 samples can typically be collected and analyzed per day.	Extensive QA/QC must be followed.
Can delineate contaminant source area and plume of VOCs.	Cannot be easily conducted in very low permeability or saturated soils.
SVOCs and heavy petroleum product contamination can be inferred indirectly by measuring products of biodegradation.	Analytical equipment selected may not be capable of identifying all constituents present.

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Passive Soil-Gas Sampling Methods

Of the two soil-gas sampling methods—active and passive—passive soil-gas sampling techniques are typically used when SVOCs or low volatility compounds are the primary constituents of concern. Passive soil-gas surveys utilize probes that are placed in the ground for days or weeks to adsorb soil-gas constituents on sorbent material using the ambient flow of vapors in the subsurface. After the probe is removed from the ground, it is sent to a laboratory where contaminants are desorbed and analyzed. An example of a passive soil-gas sampler is presented in Exhibit IV-7.

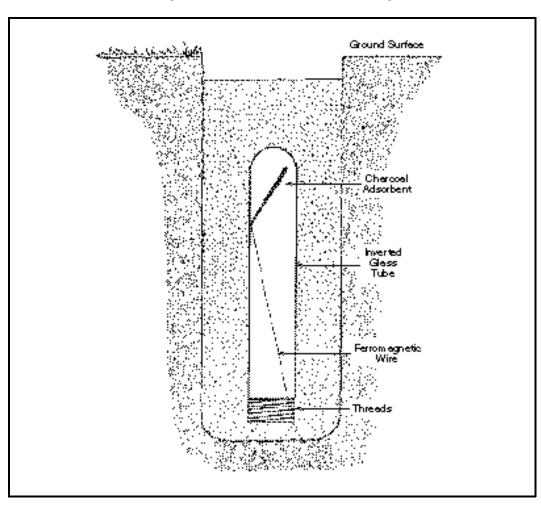


Exhibit IV-7
Example Of Passive Soil-Gas Sampler

Source: Kerfoot and Barrows, 1987

Applications For Passive Soil-Gas Sampling

Passive soil-gas surveys are not considered an expedited site assessment method because of the extended time required to collect and analyze the data. However, in certain applications, the passive devices may be used as a screening tool to help determine the soil and groundwater sampling location needed to complete a site assessment. Generally, passive sampling is most applicable when SVOCs are a primary concern, when numerous unknown compounds are suspected (*e.g.*, a Superfund site), or when subsurface conditions do not permit adequate penetration with DP methods for active soil-gas sampling. Capabilities of passive soil-gas surveys include:

- Providing an initial screening at very large sites;
- Screening the site for potential leakage from a UST or product line;
- Providing data on the types of contaminants present in the vadose zone, including a wide range of VOCs, SVOCs, and complex mixtures;
- Providing information on the lateral distribution of contaminants in the vadose zone;
- Identifying sources of contaminants; and
- Tracking a groundwater plume.

Passive Soil-Gas Survey Design

The specific survey design will vary between sites for a number of reasons including the size of the site, the survey objectives, and the capabilities of the sampler; however, some generalities can be presented. Sampling devices are placed just below the surface (between 3 inches and 4 feet) and can be quickly installed (between 2 and 15 minutes per device). A grid design is used because all sampling devices are analyzed at the same time (*i.e.*, analytical results do not affect sampling locations). The number of samples and their spacing vary but, in general, 15 to 30 samples are sufficient for a 1- to 2-acre gasoline station survey. Sampling devices are left in the ground for 3 to 21 days and then removed and typically shipped to the manufacturer's laboratory for analysis. Individuals installing the sampling devices must ensure that contamination does not occur prior to installation or after removal. Field blanks are, therefore, a necessary check on field procedures.

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Interpretation Of Passive Soil-Gas Data

A report can usually be developed 2 to 3 weeks after removal of the sampling devices. The results are reported in the amount of contaminant detected per sorbent device. It is not possible to quantify the concentration of contaminants present in the soil gas using passive sorbent devices because the volume of gas contacting the sorbent material is unknown. The relative concentrations of analytes on the sorbent may be related more to differences in the affinity of individual VOCs for the sorbent (as well as sorbent capacity for that VOC) and vapor flow rates than to the relative VOC concentrations in soil gas. In addition, passive soil-gas surveys typically collect samples from a single depth which will provide only a 2-dimensional view of contaminant distribution. Usually there is not sufficient site-specific geologic information to make a judgement about the actual distribution of contaminants. For example, perched water tables may appear as clean zones, and changes in the data may be related to changes in the thickness of clay layers rather than changes in subsurface contaminant concentrations. As a result, although passive soil-gas surveys are an effective screening method, interpretation of the data is more limited than active soil-gas surveys.

Cost Of Passive Soil-Gas Surveys

The cost of passive soil-gas surveys varies among manufacturers of sampling devices, ranging from \$75 to \$225 per sample (including analysis). Because analytical costs for UST sites tend to be on the low end of this range and because sampling 15 to 30 locations is typical for a 1-acre site, most gasoline stations can be screened for between \$1,200 and \$3,000.

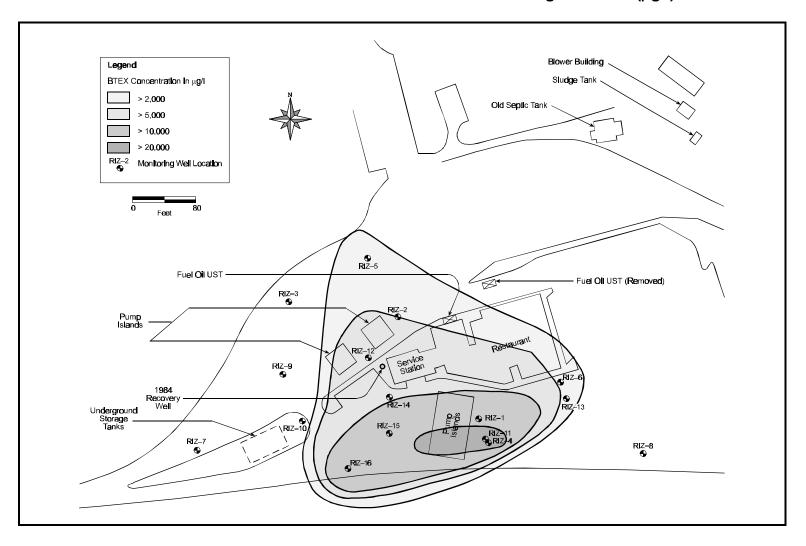
Passive Soil-Gas Survey Case Study

The following case study provides an example of the type of data that can be collected with an actual passive soil-gas survey at an UST site and how it may be interpreted. A site map is presented in Exhibit IV-8 with isoconcentration lines for BTEX in groundwater. Exhibits IV-9 and IV-10 present isoconcentration lines for diesel fuel and gasoline constituents in soil gas.

Site History

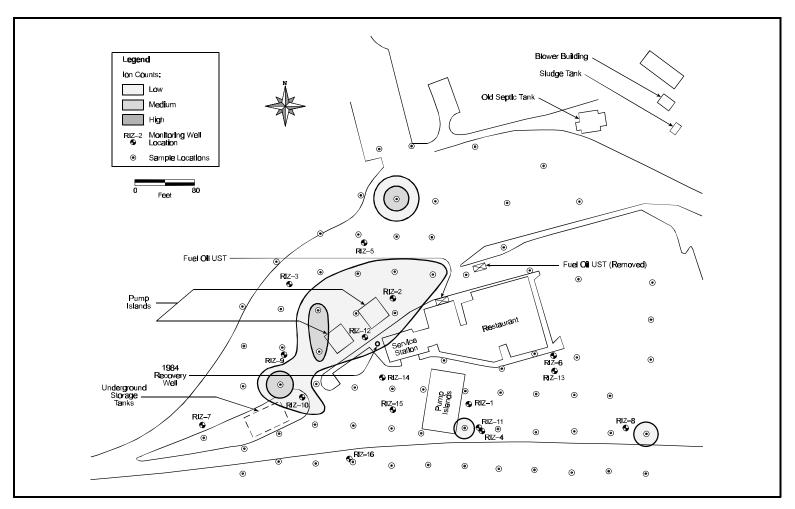
In 1990, a public highway agency began a systematic assessment of environmental site conditions at public refueling stations under its jurisdiction.

Exhibit IV-8
BTEX Distribution In Groundwater Based On Monitoring Well Data (μg/l)



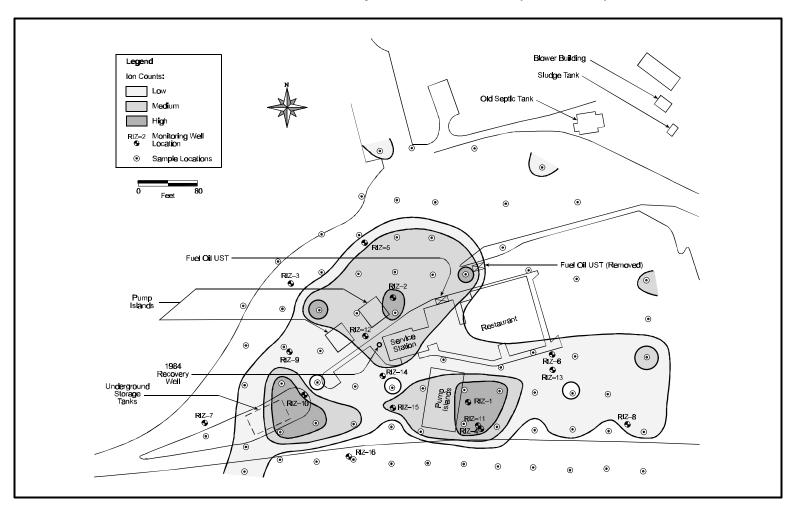
Source: Roberts et al., 1992 (Reprinted by permission of the National Ground Water Association, Westerville, Ohio. Copyright 1992. All rights reserved.)

Exhibit IV-9
Passive Soil-Gas Survey Results For Diesel Fuel Constituents
(ion counts of naphthalene and alicyclic hydrocarbons)



Source: Roberts et al., 1992 (Reprinted by permission of the National Ground Water Association, Westerville, Ohio. Copyright 1992. All rights reserved.)

Exhibit IV-10
Passive Soil-Gas Survey Results For BTEX (ion counts)



Source: Roberts et al., 1992 (Reprinted by permission of the National Ground Water Association, Westerville, Ohio. Copyright 1992. All rights reserved.)

Records at one site indicated a significant degree of contamination and warranted further investigation. Diesel fuel and gasoline USTs were replaced in 1982 and 1990. Evidence of contamination was found at both tank removals. Records suggested the potential for substantial releases throughout the site history including a potential major release of about 8,000 gallons in 1983. Sixteen monitoring wells were initially installed, and free product was discovered in four of them (Exhibit IV-8). Because the site overlaid shallow bedrock at depths between 2 and 20 feet and because of the need to delineate the SVOCs found in diesel fuel, a passive soil-gas survey was conducted.

Soil-Gas Survey Objectives

The main objective of the survey was to determine the location of the contaminant source area to facilitate remediation. The direction of plume migration was also a concern, particularly in the underlying fractured bedrock, because several drinking water wells were located within 0.5 mile.

Sampling And Analytical Methods

Eighty canisters containing ferromagnetic wires coated with active carbon adsorbent were place in a grid pattern throughout the 3 acres of the site. The canisters were left in the ground for 11 days. After the canisters were retrieved, the samples were analyzed with a gas chromatograph/mass spectrometer. Data were reported as relative flux (ion counts) for both gasoline character (BTEX) and diesel fuel character (naphthalene and alicyclic hydrocarbons).

Results And Discussion

The passive soil-gas data provided useful information about the diesel fuel source area. Exhibit IV-9 indicates that the "hot spots" are between the pump islands and the diesel fuel UST. In addition, the passive soil-gas survey correlated well with monitoring well data. Exhibit IV-10 shows that the highest BTEX concentrations were located near wells that contained floating product. Both passive soil-gas maps indicated areas that warranted additional investigation. In particular, the gasoline source area at the south end of the site appears to be centered in two locations, suggesting that the undulating bedrock might partially control the migration pattern of the petroleum compounds. Subsequent investigations with seismic refraction and boring log data supported these findings.

A summary of the advantages and limitations of passive soil-gas surveys is presented in Exhibit IV-11.

Exhibit IV-11
Advantages And Limitations Of Passive Soil-Gas Sampling

Advantages	Limitations
A wide range of VOCs, SVOCs, and low volatile mixtures can be detected.	The data cannot be used to estimate contaminant mass.
More effective than active sampling in low permeability and high moisture soils.	The vertical distribution of contaminants is typically not assessed.
From 40 to 100 devices can be installed in a day.	The time required to collect and analyze samples is typically 3 to 6 weeks.
There is minimal disturbance to subsurface and site operations.	Sorbent desorption may destroy some compounds.
Easy to install.	Measurements are time weighted and are not directly comparable to soil and groundwater laboratory methods.
	Impervious layers and changes in the thickness of clay layers can create misleading information.

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Comparison Of Soil-Gas Sampling Applications

Active soil-gas surveys are more appropriate than passive soil-gas surveys for most petroleum UST expedited site assessments because active soil-gas surveys provide more information, more rapidly, and often at a cost that is comparable to that of passive soil-gas surveys. Data collected with active soil-gas surveys can be used immediately to direct additional sampling and analysis so that the site assessment can be completed in a single mobilization. Active soil-gas surveys also provide 3-dimensional information about the distribution of contaminants and subsurface stratigraphy which allows for better interpretation of data than is possible with passive soil-gas surveys.

Passive soil-gas surveys are most useful as a screening tool when SVOCs and low volatility compounds are known or suspected to be present at a site. In addition, passive soil-gas surveys may also be useful in real estate transactions because passive soil-gas surveys provide valuable screening information which can be obtained during time-consuming negotiations without more expensive, intrusive techniques. Because of their high sensitivity to contaminant vapors, passive soil-gas surveys can provide accurate information about the specific compounds present and their relative concentration in 2-dimensions. A summary and comparison of the applications of these two soil-gas sampling methods are listed in Exhibit IV-12.

Exhibit IV-12
Applications For Active And Passive Soil-Gas Data

Application	Active	Passive
Detect presence of VOCs	✓	✓
Detect presence of SVOCs		✓
Infer assessment of hydrocarbon presence through the measurement of indicators of biodegradation	✓	
Identify specific compounds	✓	✓
Evaluate (indirectly) contaminant concentrations in soil	✓	
Evaluate 2-dimensional contaminant distribution	✓	✓
Evaluate 3-dimensional contaminant distribution	✓	
Evaluate remedial options	✓	
Monitor remedial system effectiveness	√	✓

Passive Soil-Gas Sampling Equipment Manufacturers

A list of passive soil-gas sampling equipment manufactures is included below as Exhibit IV-13. The equipment has not been evaluated by the EPA and inclusion in this manual in no way constitutes an endorsement. These vendors are listed solely for the convenience of the reader.

Because active soil-gas surveys are performed by numerous contractors throughout the country, they have not been listed here. Because these surveys are typically performed with direct push technologies, a list of active soil-gas sampling equipment manufactures is presented in Chapter V, Direct Push Technologies.

Exhibit IV-13
Passive Soil-Gas Sampling Equipment Manufacturers

PCR Laboratories	Beacon Environmental Services, Inc.
1318 East Mission Road, Suite 133	19 Newport Drive, Suite 102
San Marcos, CA 92069	Forest Hill, MD 21050
(619) 630-5106	(800) 878-5510
Transglobal Environmental Geochemistry (TEG) 13 locations across the country (800) 834-9888	W.L. Gore & Associates, Inc. 101 Lewisville Road P.O. Box 1100 Elkton, MD 21922-1100 (410) 392-3300

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References

ASTM. 1993. Standard guide for soil gas monitoring in the vadose zone, D5314-93, Annual Book of ASTM Standards, Philadelphia.

Corey, A.T. 1986. Air permeability. In *Methods of soil analysis, Part 1*, 2nd edition, A. Klute, ed., *Am. Soc. of Agron*. Monograph No. 9: 1121-36. Madison: Univ. of Wisconsin Press.

Devitt, D.A., R.B. Evans, W.A. Jury, T.H. Starks, B. Eklund, and A. Gholson. 1987. *Soil gas sensing for detection and mapping of volatile organics*, EPA/600/8-87/036. (NTIS PB87-228516).

Deyo, B.G., G.A. Robbins, and G.B. Binkhorst. 1993. Use of portable oxygen and carbon dioxide detectors to screen soil gas for subsurface gasoline contamination. *Gr. Water*, vol. 31, no. 4.

Integrated Science and Technology, Inc. 1996. Example report of soil vapor contaminant assessment. 1349 Old Highway 41, Suite 225. Marrietta, GA.

Kerfoot, H.B. and L.J. Barrows. 1987. *Soil gas measurements for detection of subsurface organic contaminants*, EPA/600/2-87/027 (NTIS PB87-174884).

Kerfoot, H.B. and P.B. Durgin. 1987. Soil-gas surveying for subsurface organic contamination: Active and passive techniques. In Superfund '87: Proceedings of the 8th national conference. Washington, D.C: The Hazardous Materials Control Research Institute.

Marrin, D.L. 1991. Subsurface biogenic gas ratios associated with hydrocarbon contamination, eds. R.E. Hinchee and R.F. Ofenbuttle. In *In-Situ Bioreclamation*, Stoneham: Butterworth-Heinemann.

Marrin, D.L. and H.B. Kerfoot. 1988. Soil gas surveying techniques. *Environ. Sci. Tech.* vol. 22, no.7: 740-45.

Marrin, D.L. and G.M. Thompson. 1987. Gaseous behavior of TCE overlying a contaminated aquifer. *Groundwater*, vol. 25, no. 1: 740-45.

Pitchford, A.M., A.T. Mazzella, and K.R. Scarbrough. 1988. *Soil-gas and geophysical techniques for detection of subsurface organic contamination*, EPA/600/4-88/019 (NTIS PB88-208194). 81 p.

- Robbins, G.A., B.G. Deyo, M.R. Temple, J.D. Stuart, and M.J. Lacy. 1990a. Soil-gas surveying for subsurface gasoline contamination using total organic vapor detection instruments: Part I. Theory and laboratory experimentation. *Gr. Water Mon. Rev.* vol. 10, no. 3: 122-31.
- Robbins, G.A., B.G. Deyo, M.R. Temple, J.D. Stuart, and M.J. Lacy. 1990b. Soil-gas surveying for subsurface gasoline contamination using total organic vapor detection instruments: Part II. Field experimentation. *Gr. Water Mon. Rev.*, vol. 10, no. 4: 110-17.
- Robbins, G.A. 1995. *Accelerated field site characterization employing 'push' technologies (II)* (With supplement gas chromatography section by B. Hartman). Short Course Notes, 4M Center, Univ. of Tennessee/Chattanooga.
- Robbins, G.A., B. E. McAninch, F.M. Gavas, and P.M. Ellis. 1995. An evaluation of soil-gas surveying for H₂S for locating subsurface hydrocarbon contamination. *Gr. Water Mon. Rev.*, vol. 15, no. 1: 124-32.
- Roberts, N., M.E. Billa, and G.E. Furst. 1992. A phased approach to remediation of a complex site. In *Proceedings of the National Ground Water Association focus conference on eastern regional ground-water issues*, Columbus, OH.
- Thompson, G.M. and D.L. Marrin. 1987. Soil gas contaminant investigations: A dynamic approach. *Gr. Water Mon. Rev.*, vol. 7, no. 2: 88-93.
- Ullom, W.L. 1995. Soil gas sampling. In *Handbook of vadose zone characterization and monitoring*, eds.L.G. Wilson, L.G. Everett, S.J. Cullen, pp.555-67. Lewis Publishers.
- U.S. EPA. 1993. Subsurface characterization and monitoring techniques: A desk reference guide. Volume 2: The vadose zone, field screening and analytical methods, EPA/625/R-93/003b. Office of Research and Development, Washington, DC.
- U.S. EPA. 1995. How to evaluate alternative cleanup technologies for underground storage tank sites: A guide for corrective action plan reviewers, EPA 510-B-95-007. Office of Underground Storage Tanks, Washington, DC.
- Werner, M.D. 1985. The effects of relative humidity on the vapor phase adsorption of trichloroethylene by activated carbon. *Amer. Indus. Hygien. Ass. J.*, vol. 46, no. 10: 585-90.

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David Ariail	U.S. EPA, Region 4
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Steve Billets	U.S. EPA, National Exposure Research Laboratory
J. Russell Boulding	Boulding Soil-Water Consulting
Gerald Church	Transglobal Environmental Geochemistry
Brendon Deyo	Horne Engineering and Environmental Services
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